WJ2.3 (Invited)
11:00 AM - 11:30 AM

Coherent anti-Stokes Raman spectroscopy on chip

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Abstract: We review possible implementations of coherent anti-Stokes Raman scattering using nanophotonic waveguide circuits. Enhancement mechanisms and limitations are discussed.

Raman spectroscopy allows for label-free detection and concentration measurement of chemicals and biomolecules. Spontaneous Raman scattering (SpRS) however suffers from a notoriously weak cross section. Various techniques exist that can boost Raman signal and hence the sensitivity of Raman spectroscopy. Among these techniques, the one using waveguides to increase the interaction length in the form of either (hollow-core) photonic crystal fiber [1] or on-chip integrated photonic wire waveguides [2] is gaining prominence. The latter scheme is a very attractive proposition for hand-held diagnostic devices as along with performance based advantages [2] it has the potential for integrating all the building blocks of a Raman spectrometer on a common platform with a very small footprint. For that reason, it is important to know how other Raman enhancement mechanisms can be combined on an on-chip platform for improving the performance of the device. Here, we particularly focus on coherent anti-Stokes Raman scattering (CARS) in coordination with cavity enhancement (CE-CARS), and surface enhancement (SE-CARS).

CARS is a nonlinear four-wave mixing (FWM) process so that the resonant enhancement comes from a coherently driven light-matter interaction. CARS has been implemented in confocal Raman microscopy for years [3] and has now reached a maturity level that has resulted in commercial products. Unfortunately, it is not trivial to transpose this technique to a chip-scale device. The reason for that is two-fold. First, CARS requires the waveguide to support twice as much bandwidth as for SpRS as both Stokes and anti-Stokes wavelengths must be guided. This is particularly difficult to achieve when the light guiding relies on a photonic bandgap such as in hollow core fibers [4]. Another difficulty is to satisfy the phase matching condition. While it can be relaxed in confocal CARS by focusing tightly, it is more difficult to phase match four-wave mixing over a broad bandwidth in a long dispersive medium. Again, in a hollow core fiber, this is difficult because dispersion-tailoring and wave-guiding are strongly correlated thus requiring to reach some kind of a trade-off between wave guidance with a reasonable loss and a low group velocity dispersion. While this also applies to nanophotonic waveguides, they certainly offer more versatility. For instance, it would be easier to implement a quasi-phase matching technique using waveguides than using optical fibers [5]. Moreover, on a fully integrated platform, it is easy to use many waveguides optimized for different parts of the spectrum. In addition to its stronger signal strength, CARS offers takes advantage from several techniques that have been developed to mitigate background noise: interferometric techniques[7], FM-AM modulation[6], and time-resolved CARS[8]. The theory for CARS in a waveguide structure is strictly equivalent to that of Kerr-based FWM. The appropriate model is thus the well-known nonlinear Schrödinger equation. Moreover, this equation has been extended to include SpRS in the context of fiber-based nonlinear optics [9] which allows to use a unique model to quantify SpRS and CARS. Fig. 1 compares CARS and SpRS signals assuming an average power of 20 mW, a 10 MHz repetition rate and a duty-cycle spanning 1 (CW) to 10^{-4} (10 ps pulse). For the sake of simplicity, we further assume a vanishing non-resonant contribution and perfect phase matching. As expected, the SpRS curve is flat over the pump pulse duration except for short pulses spectrally overlapping poorly with the Raman line. In contrast, CARS being a nonlinear process, the signal strength increases for shorter pulses as those correspond to higher peak power. Again, the advantage is mitigated for short pulses because of the bandwidth mismatch.

Surface enhanced Raman scattering relies on the plasmonic enhancement experienced by molecules in the vicinity of a metallic nanoparticle. The plasmonic resonance allows to enhance the pump and the Stokes frequencies such that the overall on-chip Raman enhancement ranges between 10^4 and 10^6 [to be published]. The progress in nanofabrication has enabled to assemble plasmonic antennas on top of

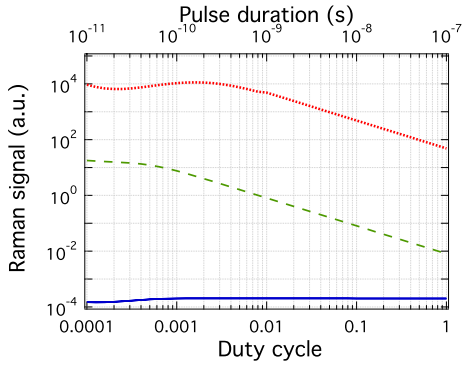

Figure 1. Comparison between SpRS (blue bold line), CARS (green dashed line) and CE-CARS (red dotted line). For the CARS and CE-CARS, the seeding spectral brightness is modest at 1mW/nm. For CARS and SpRS the waveguide length is 1 cm, for CE-CARS, the cavity diameter is 100 µm and the propagation loss is 4 dB/cm. All curves assume a fairly low Raman coefficient of 1 $W^{-1}m^{-1}$ (representative of IPA in the evanescent field of a waveguide) for a linewidth of 1 cm^{-1} (30 GHz) at a resonance frequency of 1000 cm^{-1} and a collection bandwidth of 15 cm^{-1} (1 nm).

nanophotonic structures [10]. However, antennas are tiny discrete components sampling an extremely small volume thus mitigating the overall enhancement. To further enhance the signal, CARS can be combined [11] with SERS. SE-CARS has resulted in a single molecule sensitivity [12] using triply resonant antenna and is promising on a waveguide platform as its discrete interaction solves the problem of phase matching.

While the use of cavities is well established in absorption spectroscopy as it increases the path length through a dilute analyte, this is not the case in Raman spectroscopy. For Raman spectroscopy, the situation is different as the scattering is not necessarily collinear with the pump beam thus making a cavity configuration unpractical. For guided light, one may wonder whether there is any advantage of using a cavity over an equivalently long waveguide. On resonance, a cavity enhances the pump field by a factor FE related to the Finesse by $Finesse = \pi FE^2$ assuming critical coupling. However, the cavity length L_{cav} for a given field enhancement factor is related to the effective length L_{eff} of a waveguide as $L_{cav} = L_{eff}/Finesse$. As the total spontaneous Raman power collected out of the cavity is proportional to the pump power and to the propagation length, this implies that SpRS does not benefit from any enhancement over an equivalent straight waveguide. The conclusion is dramatically different for cavity enhanced CARS as the anti-Stokes power scales as FE^8 for triply resonant modes of the cavity. In figure 1 we compare the out-coupled anti-Stokes CE-CARS signal to those obtained for CARS to SpRS for a typical microring cavity. It is important to note that the curves assume an integration over a full free spectral range of the cavity and still show an improvement over waveguide-based CARS. However, we see that the enhancement saturates for pulses shorter than 100 ps because the pump pulse bandwidth exceeds the cavity linewidth. For shorter pulses, the cavity experiences Raman parametric oscillation which isn't suitable for spectroscopy of multiple lines.

In conclusion, CARS is going to improve the Raman signal by 4 to 8 orders of magnitude over on-chip SpRS using similar photonic structures. While the resource overhead implies pulsed source and bright white light (supercontinuum, LED, or tunable laser), we believe the advantage in terms of signal to noise ratio justifies it fully. Indeed, background elimination can be implemented on CARS spectra while this is far more difficult with SpRS. In essence, CARS paves the way to an all-on-chip Raman spectroscopy.

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